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# MEMORANDUM

**TO:** Michael L. House
Manager, Remedial Projects
Solutia Inc.

**FROM:** Phillip de Blanc, Ph.D., P.E.
Robert S. Lee, P.G.

**SUBJECT:** Monitoring Well Evaluation for Remediation Effectiveness Evaluation
Solutia Nitro Facility, Nitro, West Virginia

**Via email:** mlhous1@solutia.com

## EXECUTIVE SUMMARY

Solutia Inc. (Solutia) currently monitors groundwater quality in two groundwater units at the former Flexsys America L.P. site in Nitro, West Virginia. Groundwater at the site is impacted by various organic compounds. Solutia installed slurry walls around the three source areas at the site to isolate the sources and high-concentration groundwater. Based on a request from the EPA, Solutia seeks to demonstrate the effectiveness of the remedial measures by documenting inward head gradients across the slurry walls and decreases in groundwater concentrations in its monitoring wells. Solutia requested that GSI Environmental Inc. (GSI) evaluate and/or explain:

- features of the site that affect groundwater flow patterns;
- the rationale behind the location of pumping wells inside the slurry walls;
- the number and location of gradient monitoring wells needed to demonstrate an inward hydraulic gradient across the slurry walls;
- the number and location of wells that are likely to show the most rapid concentration decreases so that they might be included in the remediation effectiveness evaluation; and,
- the overall effects of the remediation systems on groundwater concentrations.

Several features, including the location of the site adjacent to the Kanawha River, the higher transmissivity of the lower part of the alluvial aquifer, the distribution of cross-wall gradients, and the relative changes in concentration all have an effect on the locations of wells (for both pumping and monitoring). Hydraulically, cross-wall gradients are higher on the downgradient sides of the barrier walls because the natural groundwater gradient is from the center of the site to the Kanawha River. As a result of this distribution, cross-wall gradient monitoring wells and pumping wells are best located along the downgradient side of the slurry walls. The final locations of the cross-gradient monitoring wells are shown in Figure 4.

Mass transport modeling using MT3D with the existing MODFLOW groundwater flow model has identified locations where groundwater concentrations are likely to show the largest change over a 3-year period. However, the maximum concentration change for any of the new or existing wells is modest, so that dramatic changes in concentrations over the relatively brief 3-year effectiveness monitoring period are not expected. Rather, the trends in these concentrations are the more important factor in demonstrating the effectiveness of the remedial systems instead of the absolute magnitude of concentration changes. The final locations of the concentration monitoring wells are shown in Figure 14 and are listed at the end of this memorandum.

## SITE FEATURES AND CONCEPTUAL MODEL

Several features of the Nitro site have a large effect on groundwater flow patterns and the effect of the barrier walls on these patterns. Perhaps the most obvious of these features is that the Nitro site is located on the eastern bank of the Kanawha River. Along this bank, the ground surface slopes steeply downward from a height of approximately 20 to 30 feet to the water surface. The Past Disposal Area (PDA) and the West Waste Treatment Area (WTA-W) are both located nearly adjacent to this bank.

Gradients within the slurry walls are small, so that the groundwater elevation within the walls is nearly flat. Because a significant gradient is needed to force water into and out of the source areas through the walls, groundwater mounds on the outside of the upgradient side of the walls, while groundwater on the downgradient side of the walls is lower than the groundwater elevation inside the source areas.

Figure 1 illustrates this effect in the absence of pumping within the walls, while Figure 2 shows how cross-wall gradients are affected by pumping. These head gradients are in Zone A, but cross-wall gradients in Zone B are similar. Note that although the model predicts three areas of inward cross-wall gradients under pumping conditions (Figure 2), particle tracking analyses indicate that no water actually escapes from the source areas at the design pumping rates.

## PUMPING WELLS

The fact that the upgradient sides of the source areas tend to naturally exhibit an inward hydraulic gradient while the downgradient sides exhibit an outward hydraulic gradient suggests that pumping within the slurry walls near the downgradient wall will be most effective in creating an inward gradient. Flow modeling confirms that pumping wells are most effective when installed on the inside of the downgradient walls. Although the head differences within the walls are fairly small, there is a small gradient across the interior of the slurry walls. Pumping near the downgradient slurry wall lowers the head along the inside of the downgradient wall more than pumping in the middle or upgradient side, so that pumping is more efficient (rates are lower) if the wells are located near the downgradient wall.

As seen by comparing Figures 1 and 2, pumping within the walls has a large effect on the cross-wall gradients, preventing any water within the slurry walls from discharging to the Kanawha River. Even without any pumping in the slurry walls, the barrier walls have a large effect on the amount of water flowing into the Kanawha River from the source areas. With no pumping, the flow from within the barrier walls into the river is reduced by 99.65%. As the pumping rate increases, groundwater flow rates (and therefore, chemical mass) is similarly reduced, by 99.85% at 1 gpm and upwards of 99.95% at 1.8 gpm. At the design pumping rate, the mass discharge is theoretically reduced by 100% (no mass discharged into river from within the slurry walls).

Although the barrier walls will substantially reduce the long-term mass flux into the Kanawha River, some impacted groundwater will continue to flow into the river in the short term because some affected groundwater is located outside of the barrier walls. However, since the source areas are now isolated by the barrier walls, and the highest concentrations of COCs are within the source areas, the long-term mass of COCs discharging to the river will be greatly reduced.

**CROSS-WALL GRADIENT MONITORING WELLS**

The greatest outward gradient (with no pumping) and smallest inward gradient (when pumping inside the slurry walls) occurs on the downgradient side of the slurry walls. The cross-section provided in Figure 3 shows this effect at the PDA. Note that the head difference across the upgradient barrier wall is significantly greater than the head difference on the downgradient side.

This fact suggests that any failure to maintain an inward hydraulic gradient will be detected first across the downgradient side of all of the barrier walls, where the head difference is already the least. By contrast, the mounding of groundwater on the exterior of the upgradient side of the slurry walls suggests that an outward gradient is unlikely to develop at that location, or that it would manifest itself only after outward gradients had occurred on the downgradient side of the source area walls.

The smaller cross-wall gradients occurring on the downgradient side of the barrier walls suggest that cross-wall gradient wells located on the downgradient walls would be leading indicators of gradient changes across the walls at other locations. Therefore, as shown in Figure 4, cross-gradient monitoring wells have been located along the downgradient wall sections in all source areas.

It is possible that, at some times of the year, the gradient across the slurry walls could reverse from inward to outward. The head in the Kanawha River is maintained at a constant elevation of 566 ft msl. If heavy rainfall creates an increased head in the bedrock aquifer recharge areas, the gradient across the site could increase because of the constant river stage. This increased gradient could raise bedrock aquifer heads inside the slurry walls. The effect would likely be greatest in the PA and WTA-E, which are located further from the river than the other two units. Such a gradient reversal would be expected to be temporary as heads in the bedrock aquifer subside.

The gradient across the walls could also reverse if the Kanawha River stage were lowered for a substantial period of time. The reduced river level would lower the groundwater elevations on all sides of the barrier walls. However, water levels in the adjacent Kanawha River are maintained by the US Army Corps of Engineers to provide a navigable waterway for recreation and commerce. The Nitro site is situated along the lower portion of the Winfield Locks pool where fluctuation in river operating levels is minimized. The flow within the Kanawha River is regulated by controlling discharges from three storage reservoirs situated within the watershed. These include

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Summersville Lake (on the Gauley River), Sutton Reservoir (on the Elk River), and Bluestone Dam. Discharge flows from these facilities are regulated to maintain a minimum pool level. As a result, only rarely would the river levels drop significantly below the normal pool level of 566 feet representative of the Winfield pool.

Outward hydraulic gradients could also occur if there is localized poor contact between the barrier walls and the underlying bedrock surface so that underflow occurs beneath the walls, or if localized tears or rips in the cap liner allow substantial recharge within the barrier walls. Solutia has taken measures during construction of the barrier walls and will take measures during caps and covers installation to minimize these items.

For instance, installation of the barrier walls was based on an extensive subsurface exploration program to determine not only the depth of the underlying bedrock surface along the perimeter of the barrier walls, but also analysis of core samples from these areas. Numerous core samples were obtained, visually observed, and tested to determine appropriate depth of the barrier wall key excavation. During the excavation of the barrier wall keys, cuttings were compared to the samples collected to ensure that the walls were keyed into the bedrock at the proper depth.

The synthetic capping materials will be installed under a stringent quality assurance program. The quality assurance program will include visual observations of the capped surface prior to backfill, checking for any tears or defects to the material, as well as both field and destructive testing of the completed field welded seams. This construction quality assurance program will serve to minimize the potential for rips, tears, and leakage through the finished cap.

If necessary, pumping rates inside the barrier walls could be temporarily increased to compensate and maintain or re-establish an inward hydraulic gradient if any of the scenarios above were to develop.

To understand how seasonal variations in groundwater elevations affect cross-wall gradients, it is suggested that water level elevations be measured monthly for the first year. Based on this data, either semi-annual or quarterly monitoring should provide sufficient data to ensure that inward hydraulic gradients are being maintained. Monitoring times for subsequent monitoring can be set to coincide to times when cross-wall gradients are greatest and least.

## CONCENTRATION MONITORING WELLS FOR EFFECTIVENESS EVALUATION

GSI evaluated the rate of concentration changes in the wells by performing mass transport simulations of chemicals present in the groundwater, and observing locations with the greatest rate of concentration decrease. The existing groundwater flow model developed for the site was used as a basis for the mass transport model. Historical concentration contour maps and current groundwater concentration data were used to establish initial concentrations of a subset of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and pesticides/herbicides/PCBs (PEST).

GSI used the Nitro site MODFLOW (McDonald and Harbaugh, 1983) groundwater flow model developed by GSI (GSI, 2011) as the basis for the monitoring well evaluation.

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Estimated current concentrations of VOCs, SVOCs and PEST were input into the model. An MT3D (Zheng, 1990) mass transport simulation was then performed to determine the monitoring wells in which groundwater concentrations changed most rapidly following slurry wall construction.

It is important to note that this modeling exercise is conducted only for the purpose of estimating the *relative rate of concentration change* in monitoring wells. The simulation results are not intended for predicting actual concentrations of individual chemicals or chemical classes at particular locations at particular times, nor is this mass transport model suitable for such a purpose. Depictions of concentration plumes are provided only for comparison of concentration changes over the life of the simulations, and do not show the actual current distribution of chemicals in groundwater at the site.

***Estimation of Current Concentrations***

Concentration contour maps for total VOCs, total SVOCs, and total PEST from the 2003 site investigation (Potesta, 2003) were used in conjunction with the individual well concentrations to establish initial total concentrations. Concentration observation points were placed along the contour lines of the figures and treated as concentration observations. These concentration observations from the contour maps were combined with the well concentrations and imported into GMS (Groundwater Monitoring System, Build June 9, 2006; managed by Environmental Modeling Systems, Inc.) for interpolation into a continuous distribution of total VOC, SVOC, and PEST groundwater concentrations.

Because the site investigation concentration contour maps do not indicate a contour for a zero (or non-detect) concentration, an outer contour representing a zero concentration was created for each chemical class. The zero concentration contour was necessary to prevent interpolation and/or extrapolation of concentrations beyond a reasonable distance from source areas. The zero concentration contour was created at an approximate distance of 50 to 100 feet outside of the minimum contour shown for each chemical class. Concentration observation points at which the concentration was assumed to be zero were placed along these estimated zero concentration contours in the same manner as the points placed along the other concentration contours.

Well data from Zone A was combined with the contour map observation data to create the concentration datasets for model layer 1. Well data from Zone B was combined with the contour map observation data to create the concentration datasets for model layers 2 and 3. Concentration observations in wells northeast of the wastewater treatment areas were not used in the interpolations, and other isolated concentrations were similarly excluded from the datasets. Some adjustments to the concentration contour data points created from the site investigation contour maps were also made to accommodate concentrations observed in wells nearby but outside of concentration contours.

The concentration datasets were imported into GMS and interpolated to a 50-ft square grid using natural neighbor interpolation with a constant nodal function. The interpolated concentrations were exported from GMS and converted to a format consistent with the

Groundwater Vistas (GWV; Version 6.14, Build 16; created by Environmental Modeling Systems, Inc) site model.

***Mass Transport Simulation Parameters***

Mass transport simulations were performed with MT3D through the GWV interface. The interpolated total VOC, SVOC and PEST concentrations were imported into GWV and specified as initial concentrations. These three total concentrations were also specified as three "chemical species" in the MT3D model.

When transported in groundwater, organic chemicals adsorb to organic matter in the subsurface so that the rate of chemical transport is less than the rate of groundwater flow. The retardation factor (R) represents the factor by which chemicals in groundwater move slower than the groundwater itself. Because the VOC, SVOC, and PEST "species" actually consist of the total concentration of a number of different compounds, each with a different value of R, it was necessary to determine a representative value of R for the three compound classes. The representative value for each class was taken as the arithmetic average of the computed retardation factors for compounds within the class. The retardation factor for each compound was computed as:

$$R = 1 + \frac{\rho_b K_d}{n} \quad where\ K_d = f_{oc} K_{oc}$$

and: R = retardation factor (dimensionless);
$\rho_b$ = soil bulk density ($M/L^3$);
$K_d$ = soil/water partitioning coefficient ($L^3/M$);
n = total porosity (dimensionless).
$f_{oc}$ = fraction of organic carbon in the aquifer (dimensionless);
$K_{oc}$ = organic carbon/water partitioning coefficient ($L^3/M$).

MT3D uses a single porosity value to calculate both seepage velocity and the retardation factor. In reality, seepage velocity is a function of effective porosity while retardation is a function of total porosity. To correct for this characteristic of MT3D, the calculated $K_d$ values were multiplied by the ratio of ($n_e/n$) so that the combination of seepage velocities and retardation factors correctly predict chemical velocities. The calculated $K_d$ and R values for each of the three species and layers were:

| Species | Layer 1 | Layer 2 | Layer 3 |
|---|---|---|---|
| ***Kd (L/mg)*** | | | |
| VOC | 0.098 | 0.179 | 0.004 |
| SVOC | 0.121 | 0.222 | 0.005 |
| PEST | 0.053 | 0.097 | 0.002 |
| ***R (dimensionless)*** | | | |
| VOC | 1.78 | 1.96 | 2.28 |
| SVOC | 1.96 | 2.19 | 2.59 |
| PEST | 1.42 | 1.52 | 1.7 |

Values of the parameters on which these $K_d$ and retardation factors are based, and other mass transport parameters used for the mass transport simulations, were as follows:

| Parameter | Layer 1 | Layer 2 | Layer 3 |
|---|---|---|---|
| Organic carbon fraction | 0.002 | 0.002 | 0.00005 |
| Total porosity | 0.4 | 0.35 | 0.01 |
| Effective porosity | 0.2 | 0.32 | 0.009 |
| Bulk density | 1.59 | 1.72 | 2.62 |
| Longitudinal dispersivity | 12 | 12 | 12 |
| Transverse dispersivity | 2.4 | 2.4 | 2.4 |
| Vertical dispersivity | 0.24 | 0.24 | 0.24 |

Mass transport simulations were run for a period of 3 years. Advective transport was simulated using the modified method of characteristics (MMOC). A Courant number of 0.5 was specified for automatic time step control in the mass transport simulations. All degradation rates were assumed to be zero over the short period of the simulations.

***Identification of Locations Exhibiting Maximum Rate of Concentration Decrease***

The VOC "species" was used to determine the locations of most rapid concentration changes. To determine the locations that would exhibit the greatest concentration change over the 3-year period, concentration observation points were placed throughout the VOC plume in the model. Figures 5 through 8 show the locations of greatest concentration changes in terms of percent change over the next 3 years for Zones A and B in the southern and northern areas of the site. The green "0s" indicate that concentrations increased at that location, while red negative numbers indicate a concentration decrease, with the number indicating the percent decrease.

As seen in Figures 5 through 8, concentration observation points placed immediately outside of the downgradient barrier walls generally do not show the most rapid concentration decreases. The reason for the slow concentration changes at these locations is that groundwater along the sides of the source areas, while outside of the source areas, still exhibits relatively high concentrations. This groundwater flows down the sides of the exterior of the barrier walls and converges on the downgradient exterior side, transporting fairly high concentrations of constituents to these locations. In addition, groundwater flow rates immediately downgradient of the walls are relatively low, so that only slow changes in concentrations are expected at these locations.

As an example, the flowpaths around the PA are shown in Figure 9. The lines trace the path of groundwater around the source area. The small arrows on the pathlines mark 10-year travel distances. As seen in the figure, flow lines converge on the downgradient side of the PA barrier wall. The time markers are also closer together at the downgradient wall, indicating slower groundwater flow. The small concentration changes on the outside of the downgradient barrier walls is confirmed by the concentration changes provided in Figures 5 through 8.

An exception may be observation points downgradient of the WTA-E source area. Several observation points outside of the downgradient wall at this unit exhibit fairly large concentration changes. At this location, the initial high concentrations in the groundwater are displaced by lower concentrations flowing along the walls of the WTA units.

The greatest concentration changes are predicted to occur in observation points in which initial concentrations were high but where upgradient concentrations are lower. The largest concentration changes in high-concentration locations may be partially an artifact of the interpolation process, which tends to decrease concentrations as the distance from the high-concentration points increases. Generally, the simulations predict that concentrations in observation points on the upgradient edge of the plumes will decrease more rapidly than locations in the center of the plume.

Figures 10 through 13 show the names of the observation points that exhibit the concentration changes illustrated in Figures 5 through 8. Figure 14 shows the location of the observation points that are likely to be most useful for effectiveness monitoring, using both the modeling results and professional judgment. These wells are listed below:

| Wells Exhibiting the Most Rapid Concentration Change (Based on VOC Concentrations) | Source Area | New or Existing |
|---|---|---|
| CMW-11-A/B | PDA | New |
| CMW-41-A/B | WTA-E | New |
| CMW-52R-A/B* | PDA | New |
| CMW-59-A/B | PA/PDA | New |
| GW-13A/B | WTA-W | Existing |

* Location CMW-52R-A/B is slightly northwest of the CMW-52-A/B to accommodate site limitations.

These wells are supplemented by the existing concentration monitoring wells at the site. Although concentrations are expected to change only slowly at the site, sufficient data must be collected over the 3-year period to detect concentration trends. Quarterly monitoring of the monitoring wells is suggested to ensure that enough data is collected to provide a statistically significant measure of concentration changes in the wells.

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## REFERENCES

GSI, 2011. Groundwater Model Development and Flow Simulations, Solutia Nitro Site Nitro, West Virginia, GSI Environmental Inc., September 9, 2011.

McDonald and Harbaugh, 1983. A Modular Three-Dimensional Finite-Difference Ground-Water Flow Model, Michael G. McDonald and Arlen W. Harbaugh, USGS Open-File Report 83-875, 1983.

Potesta, 2003. Site Investigation of the Former Flexsys America I.P., Nitro, West Virgina Facility, Potesta & Associates, Inc. December, 2003.

Zheng, C., 1990. MT3D, A modular three-dimensional transport model for simulation of advection, dispersion, and chemical reactions of contaminants in groundwater systems, Report to the Kerr Environmental Research Laboratory, US Environmental Protection Agency, Ada, OK.

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6 March 2013

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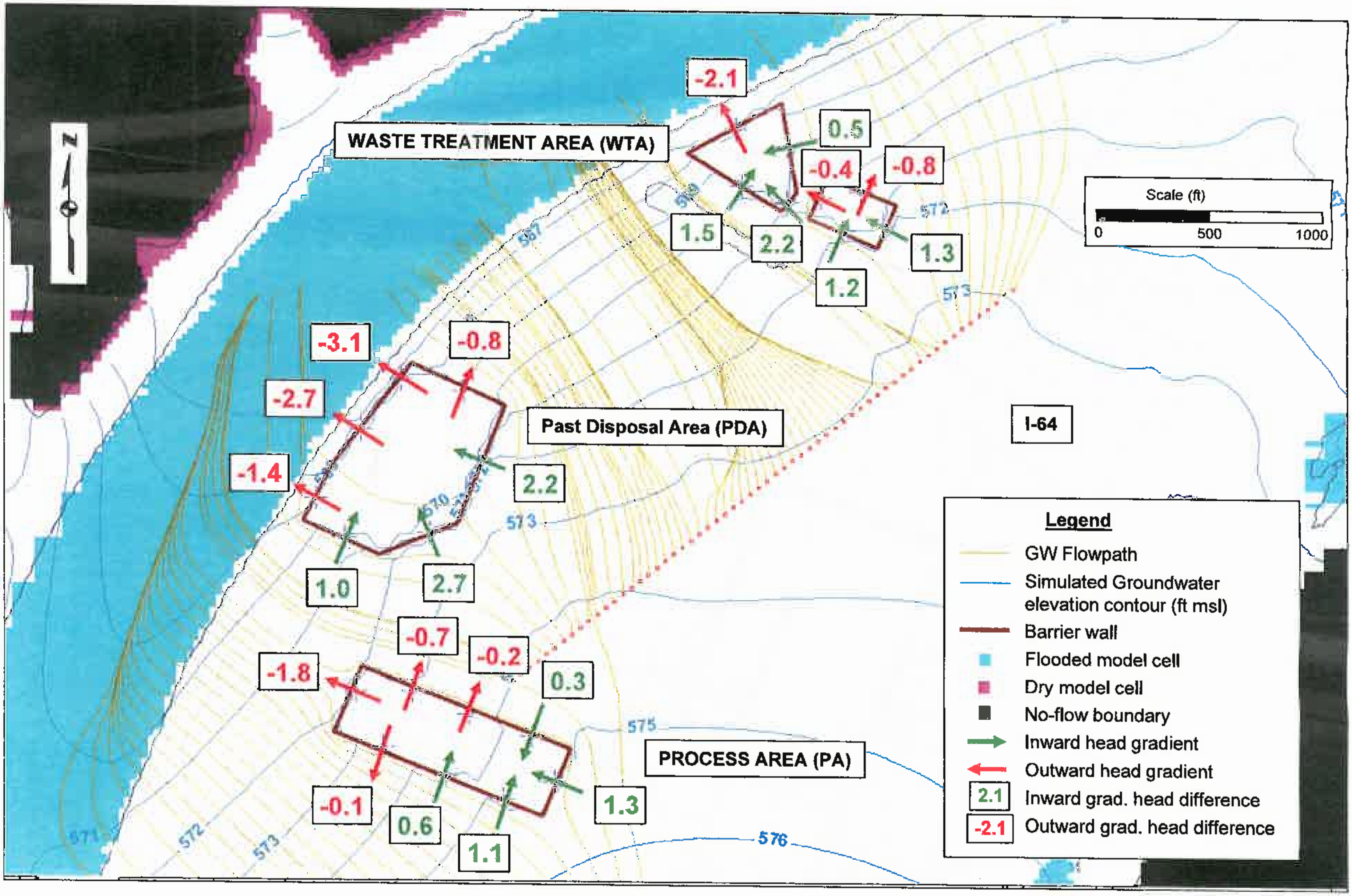
**Figure 1**
**Simulated Gradient Across Slurry Walls with Caps in Place; No Pumping**



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# Figure 2
## Simulated Gradient Across Slurry Walls with Caps in Place; with Pumping Inside Barrier Walls

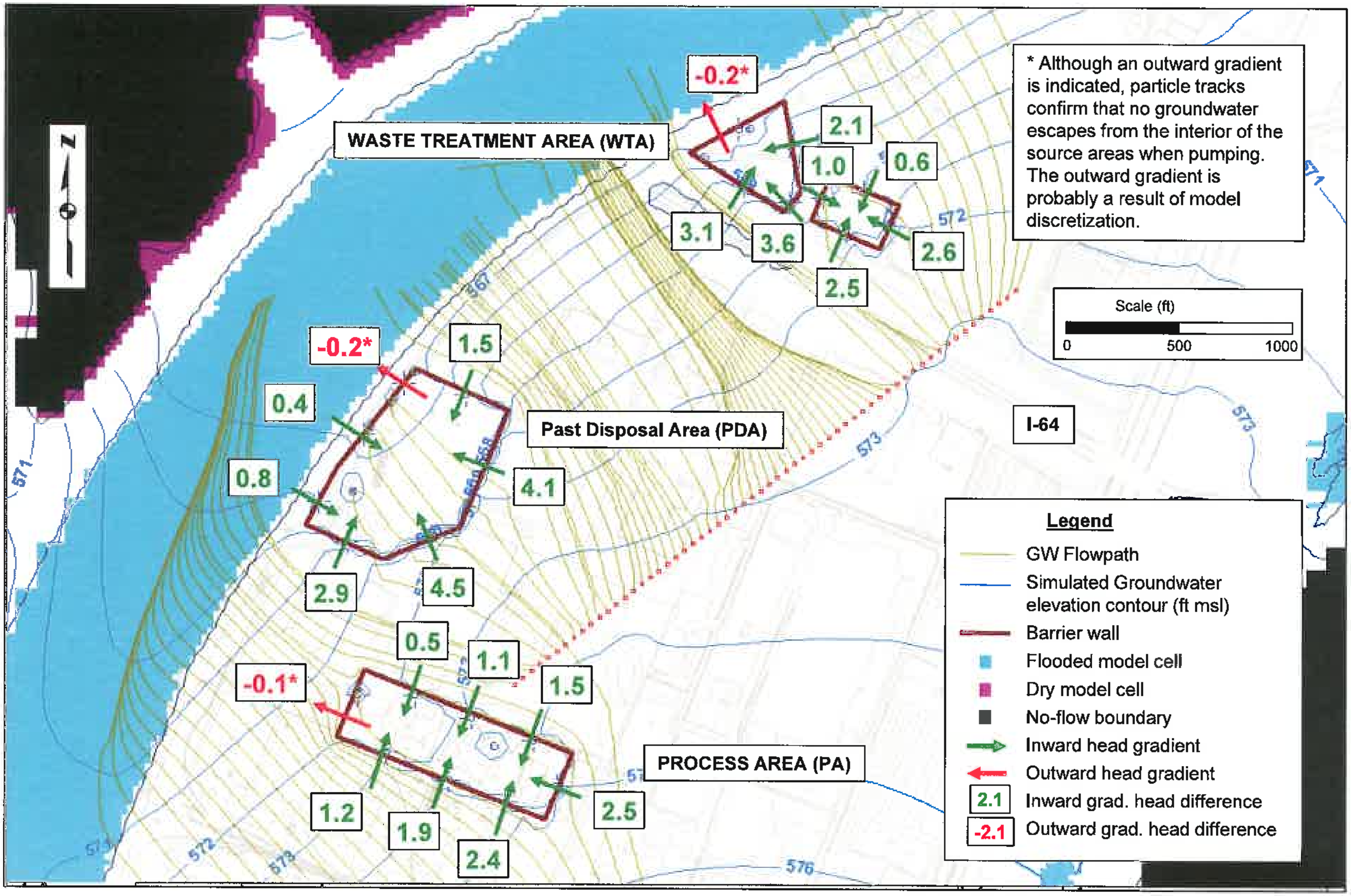

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**Figure 3**
**Cross-Sectional View of Simulated Water Table Across PDA at Model Row 194**

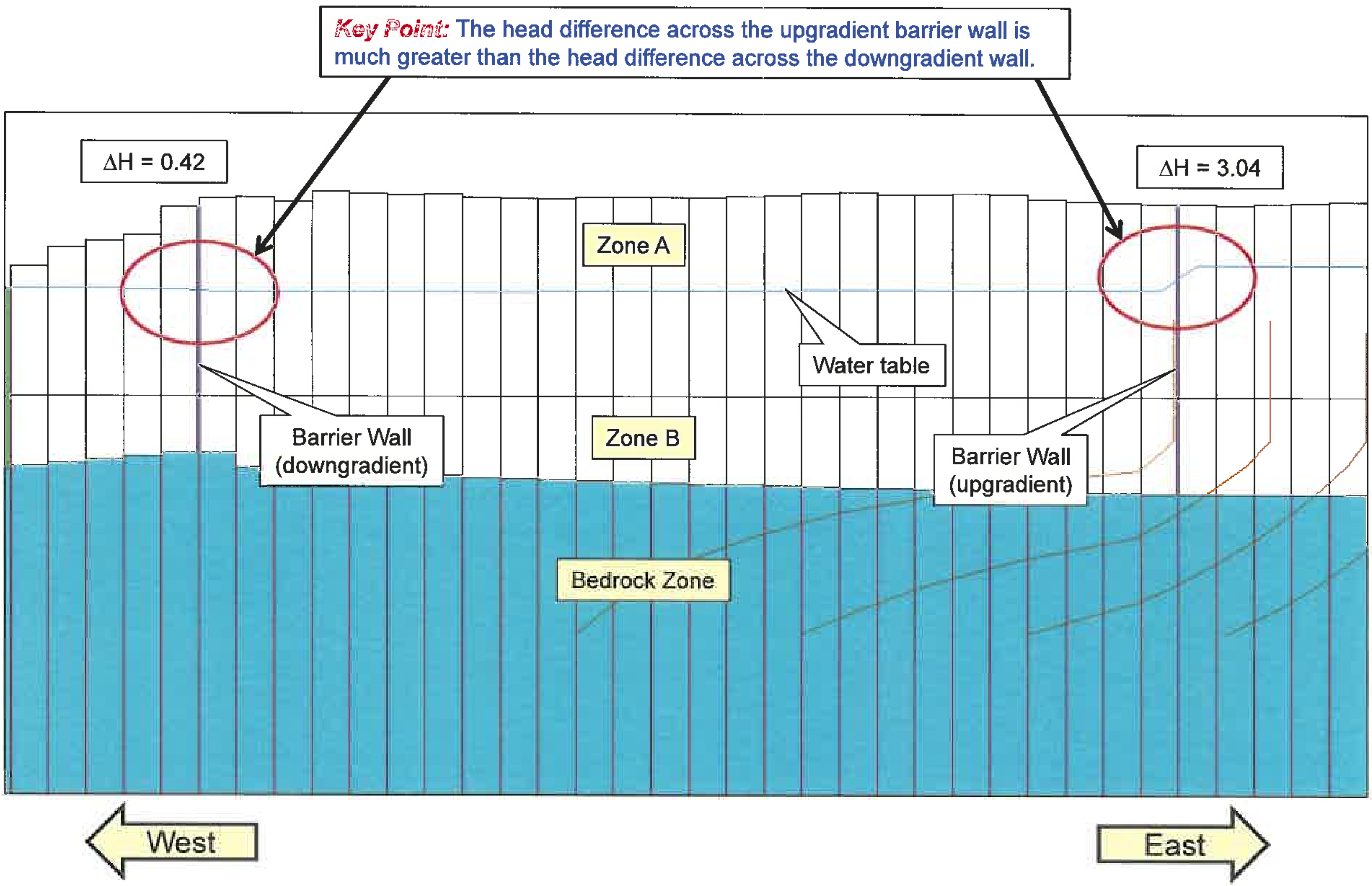

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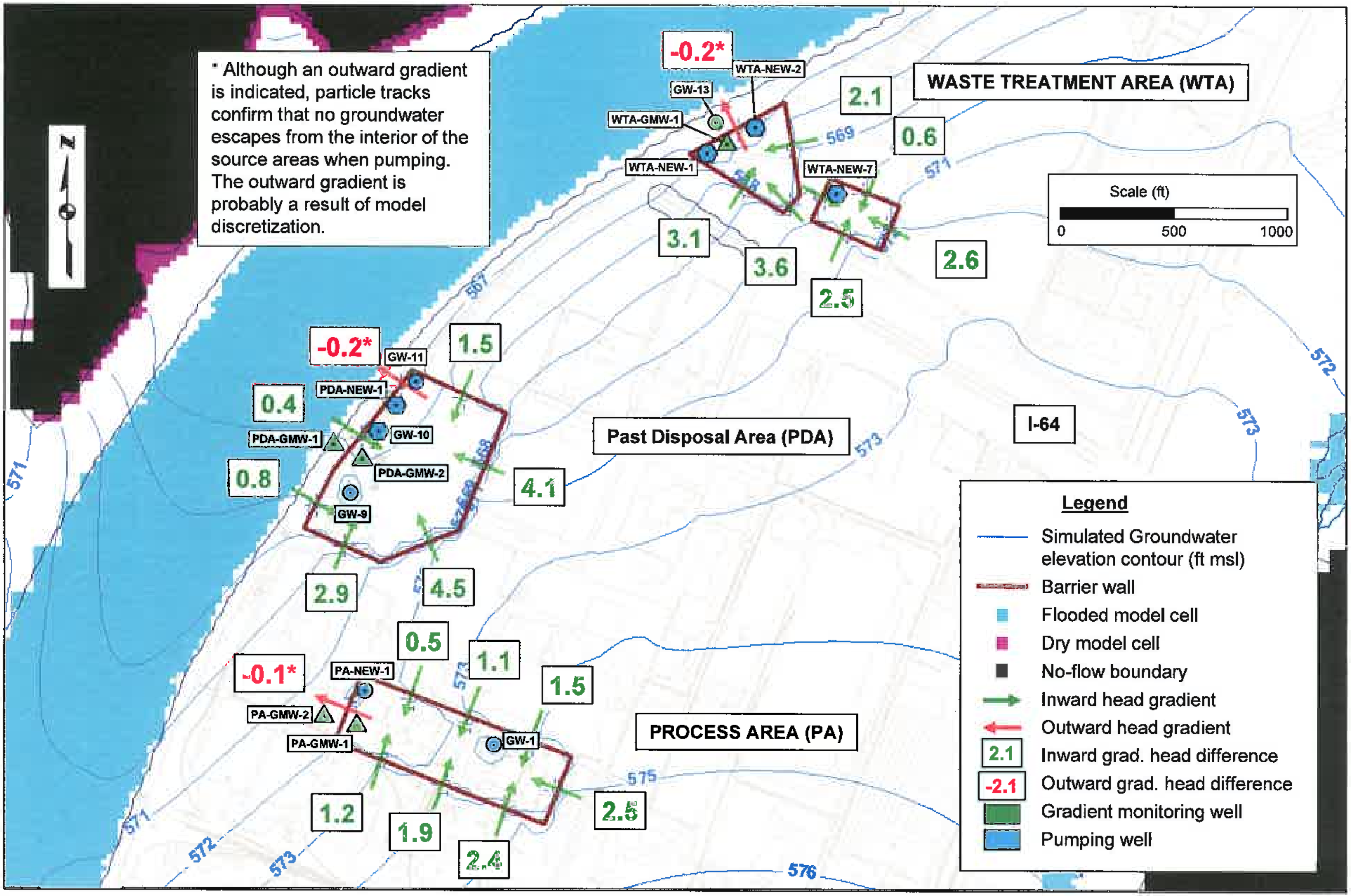
**Figure 4**
**Current Proposed Cross-Barrier Gradient Monitoring Locations**



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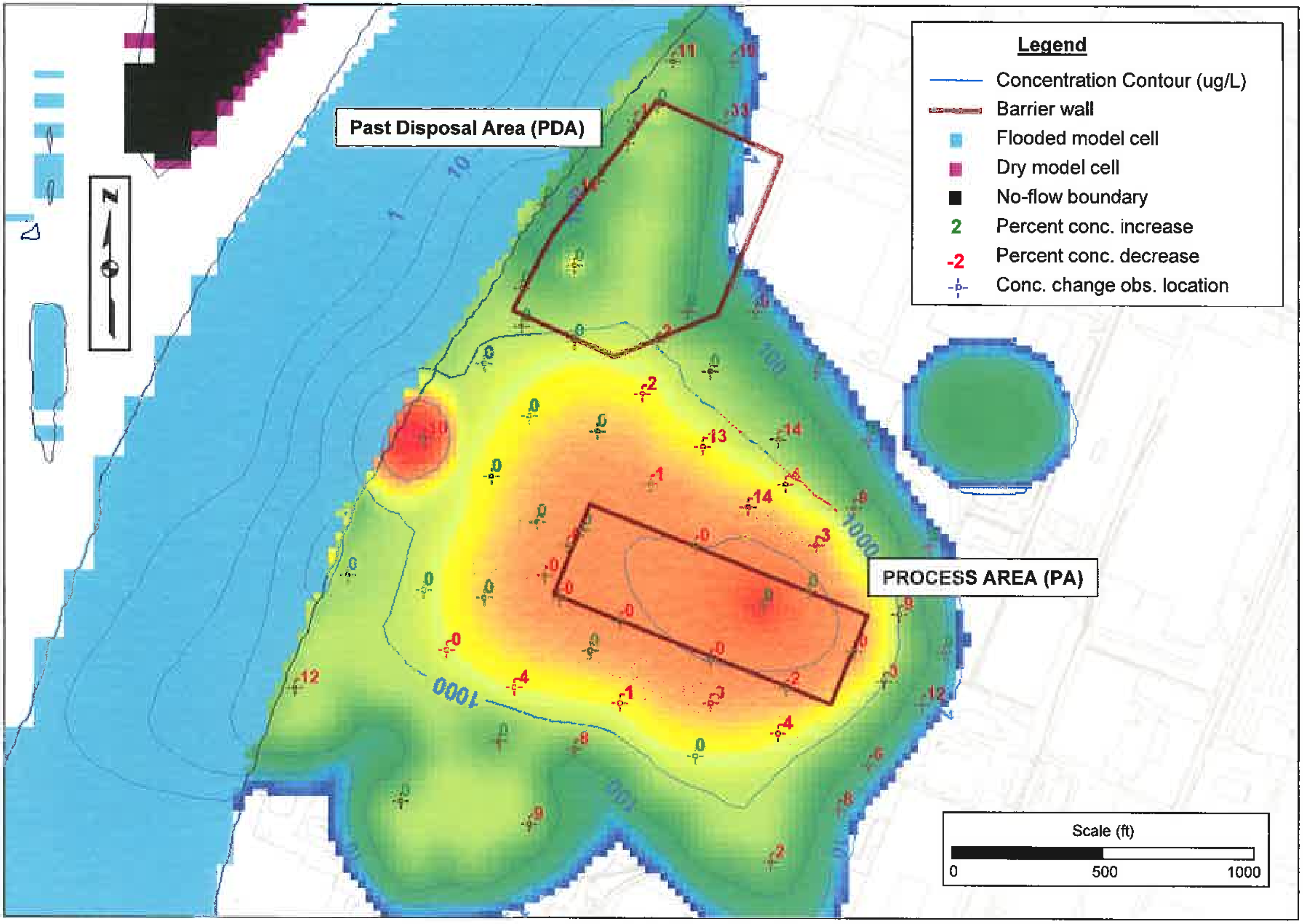
# Figure 5
## Simulated Percent VOC Concentration Change in Zone A Over 3 Years at the PDA and PA



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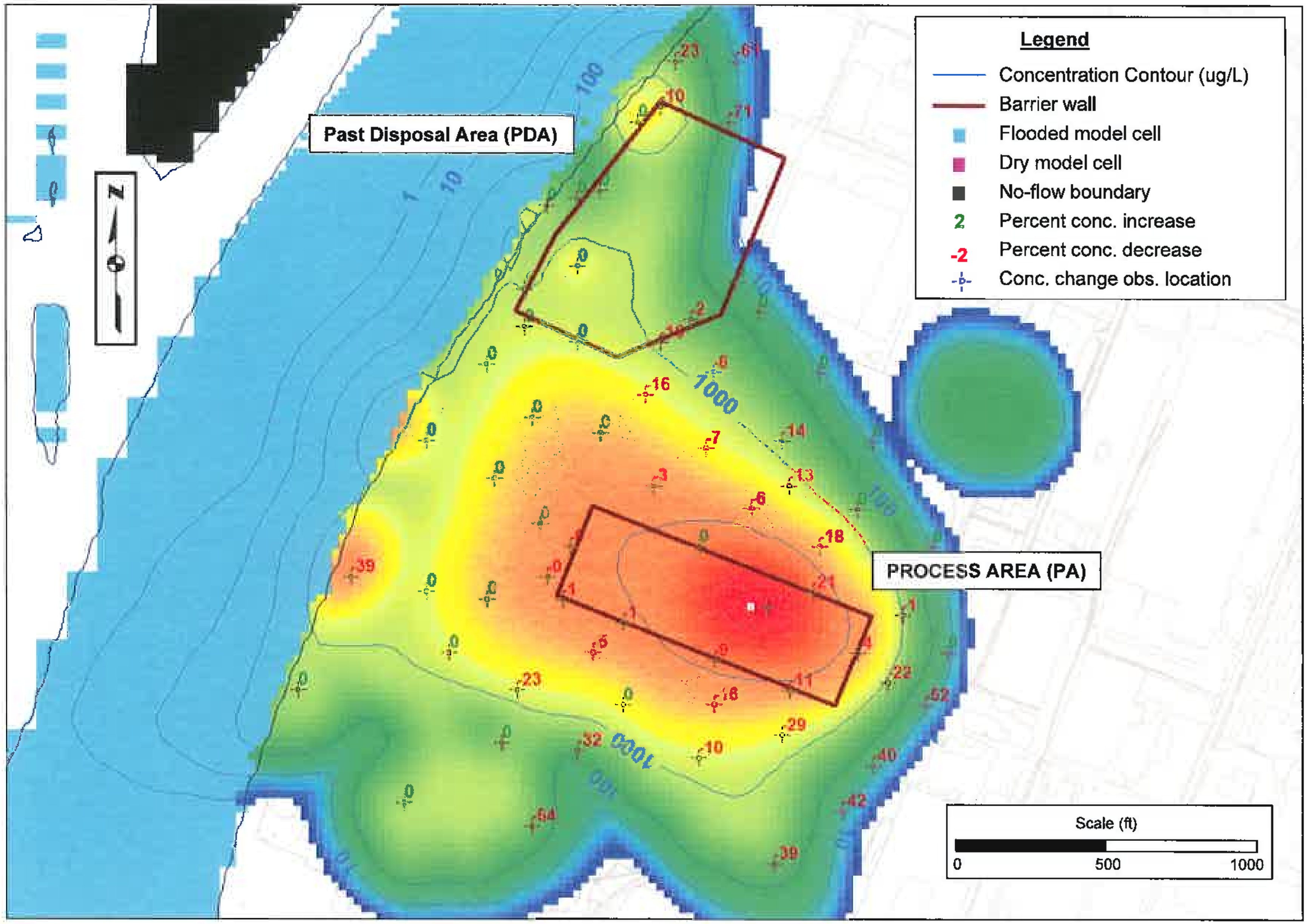
# Figure 6
## Simulated Percent VOC Concentration Change in Zone B Over 3 Years at the PA and PDA



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# Figure 7
## Simulated Percent VOC Concentration Change in Zone A Over 3 Years at the WTA

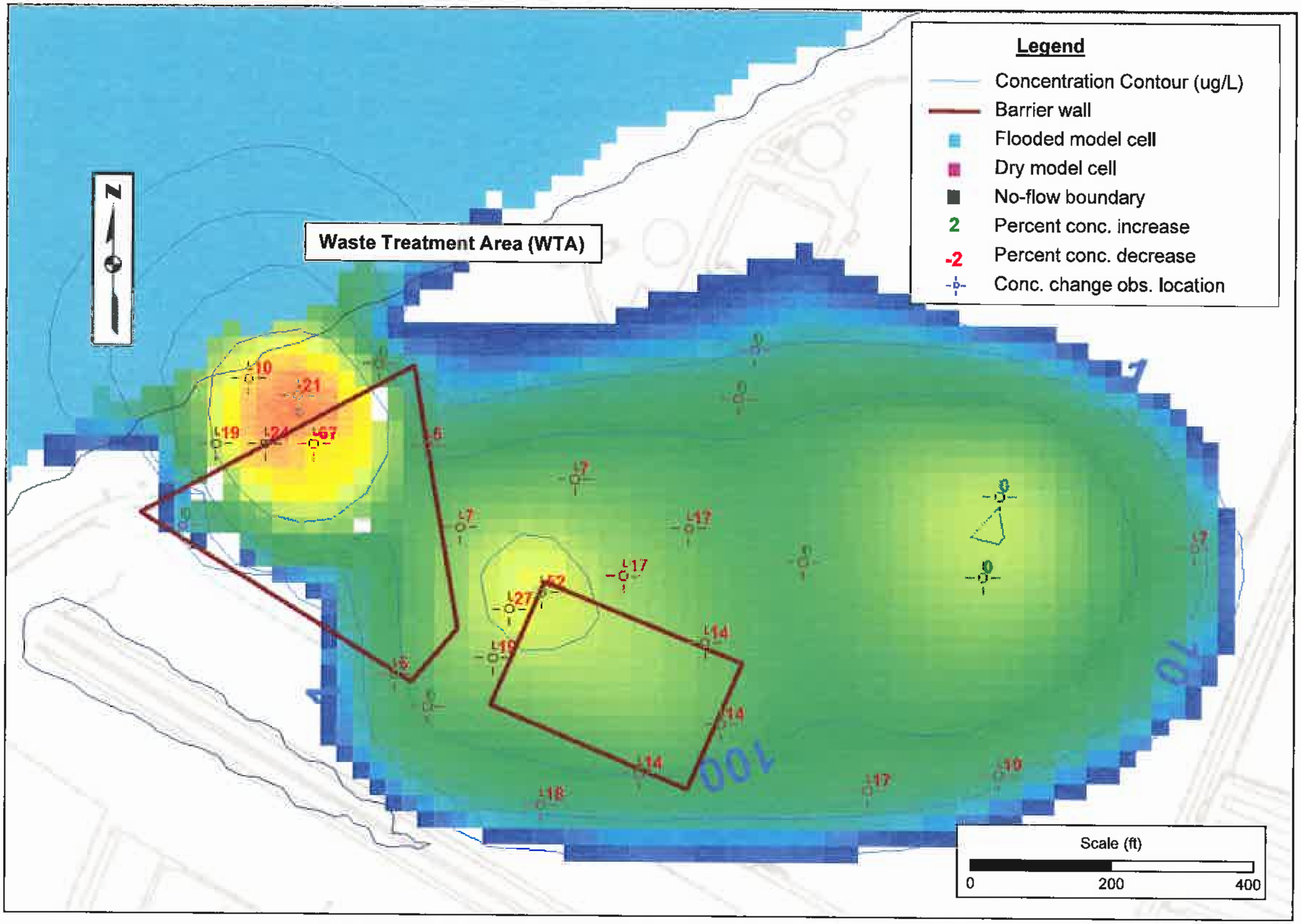


**Figure 8**
**Simulated Percent VOC Concentration Change in Zone B Over 3 Years a the WTA**

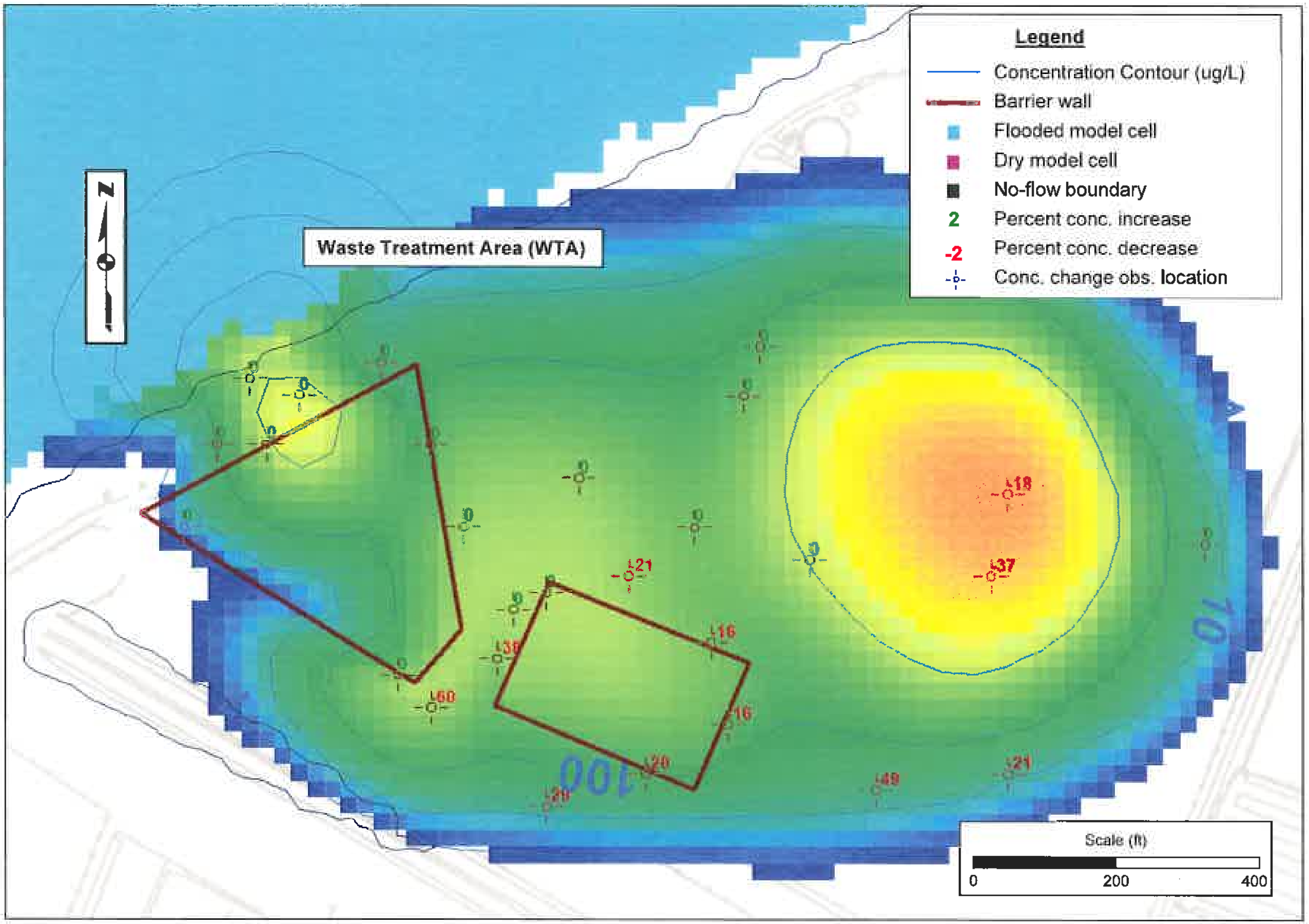
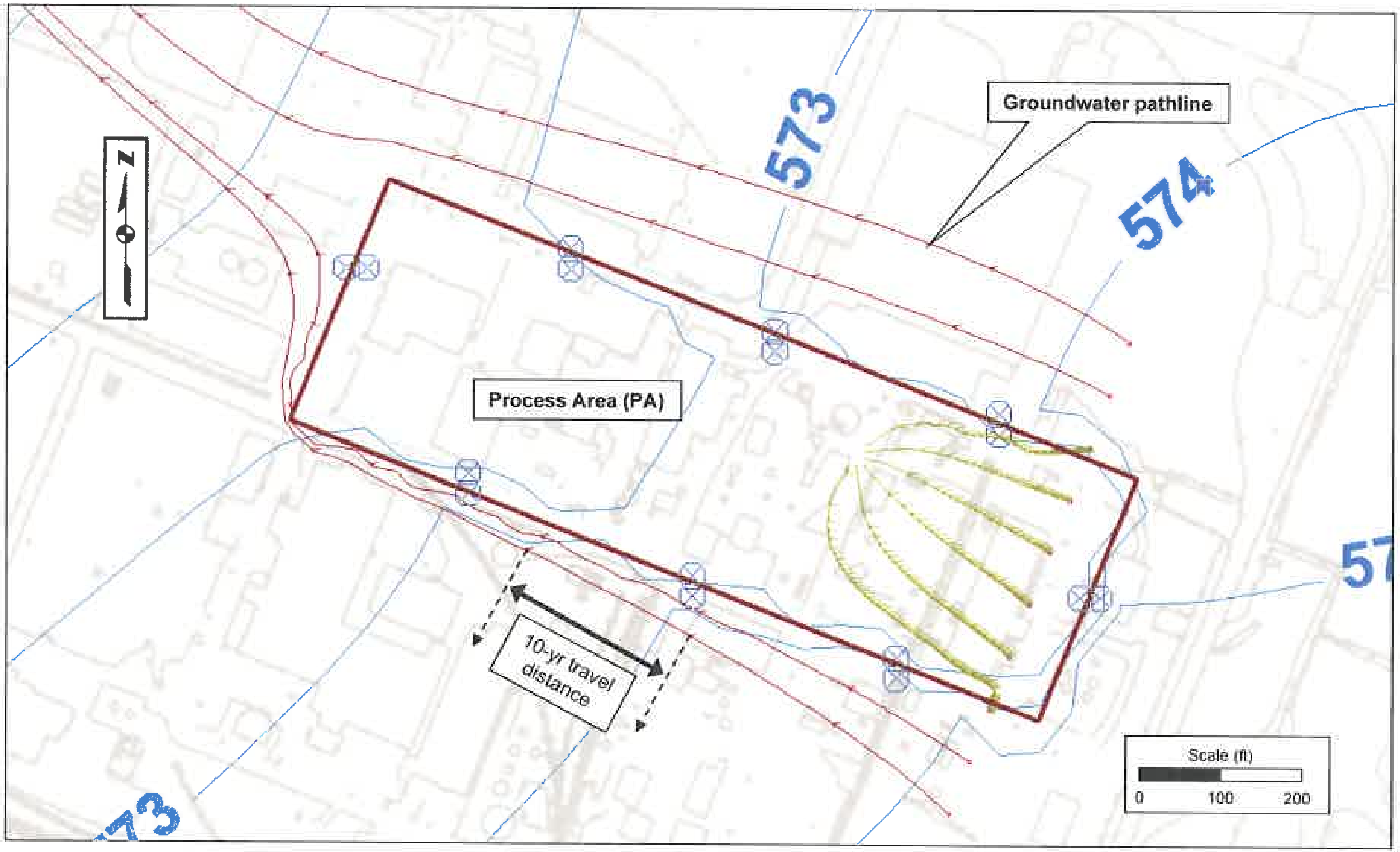


**Figure 9**
**Simulated Groundwater Flow Path Around Barrier Walls of the PA With Time Markers at 10-Year Intervals**



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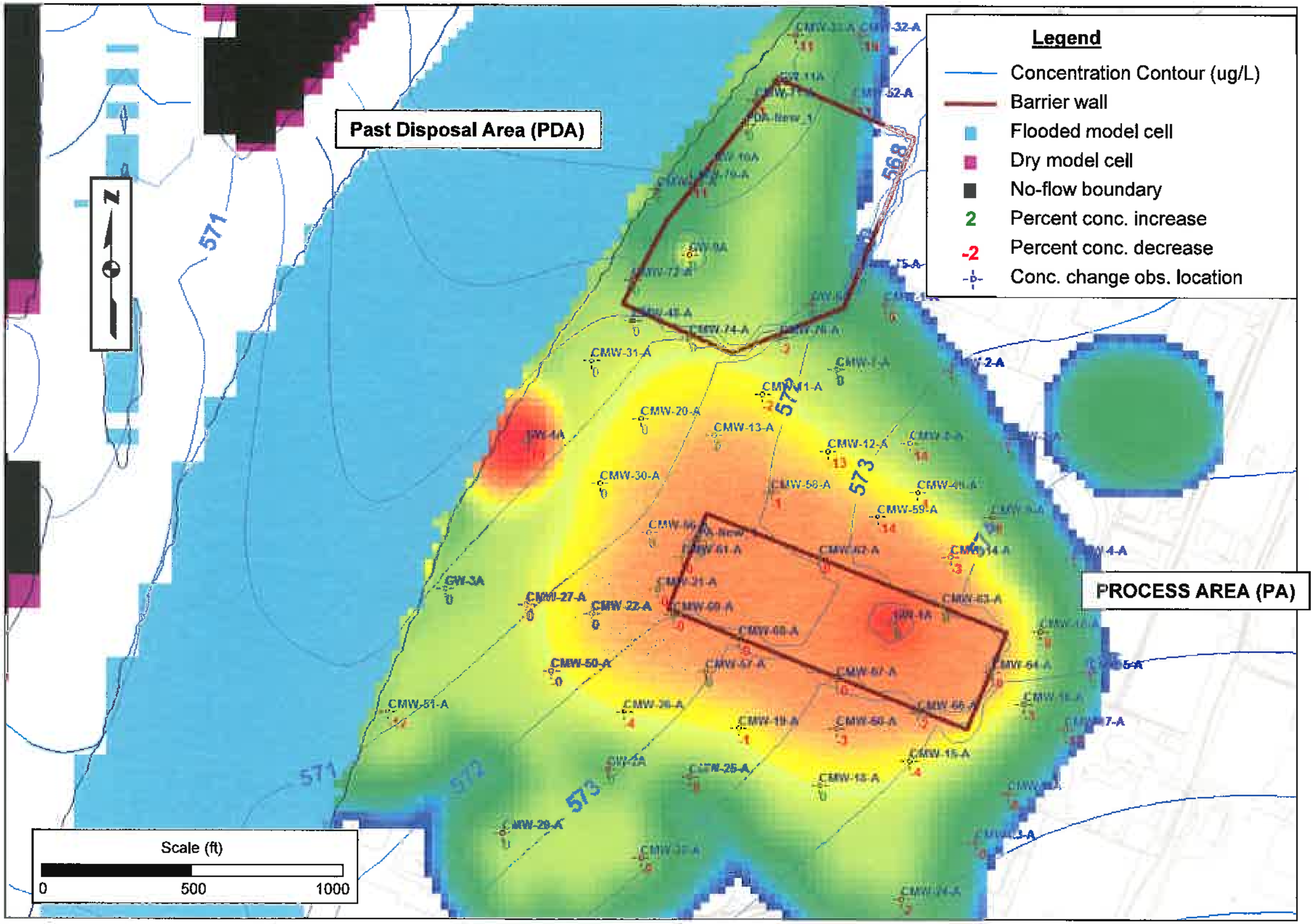
# Figure 10
## Location of Wells Corresponding to VOC Concentration Changes in Zone A at the PDA



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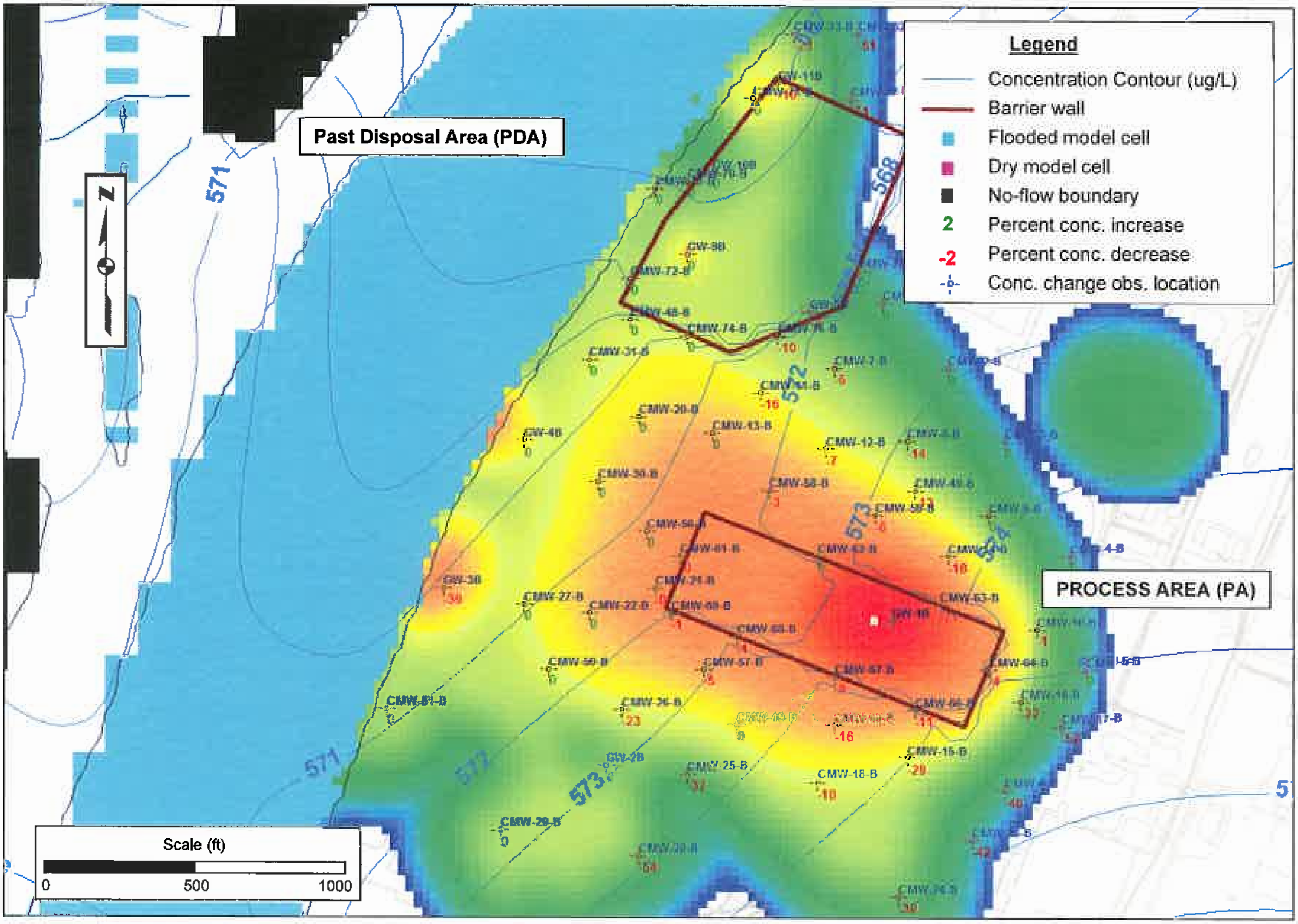
# Figure 11

## Location of Wells Corresponding to VOC Concentration Changes in Zone B at the PDA



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## Figure 12
## Simulated Percent VOC Concentration Change in Zone A Over 3 Years at the WTA

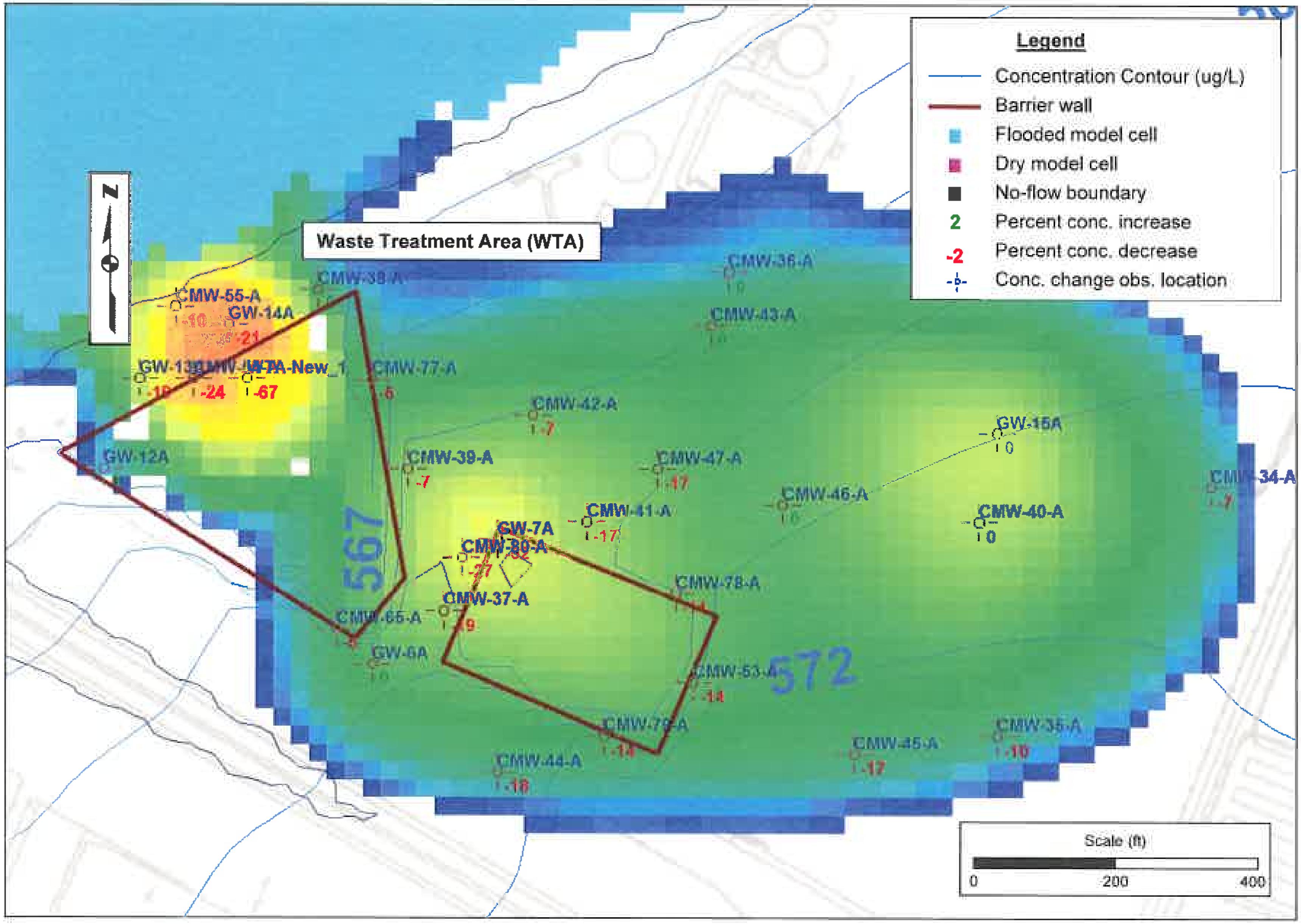

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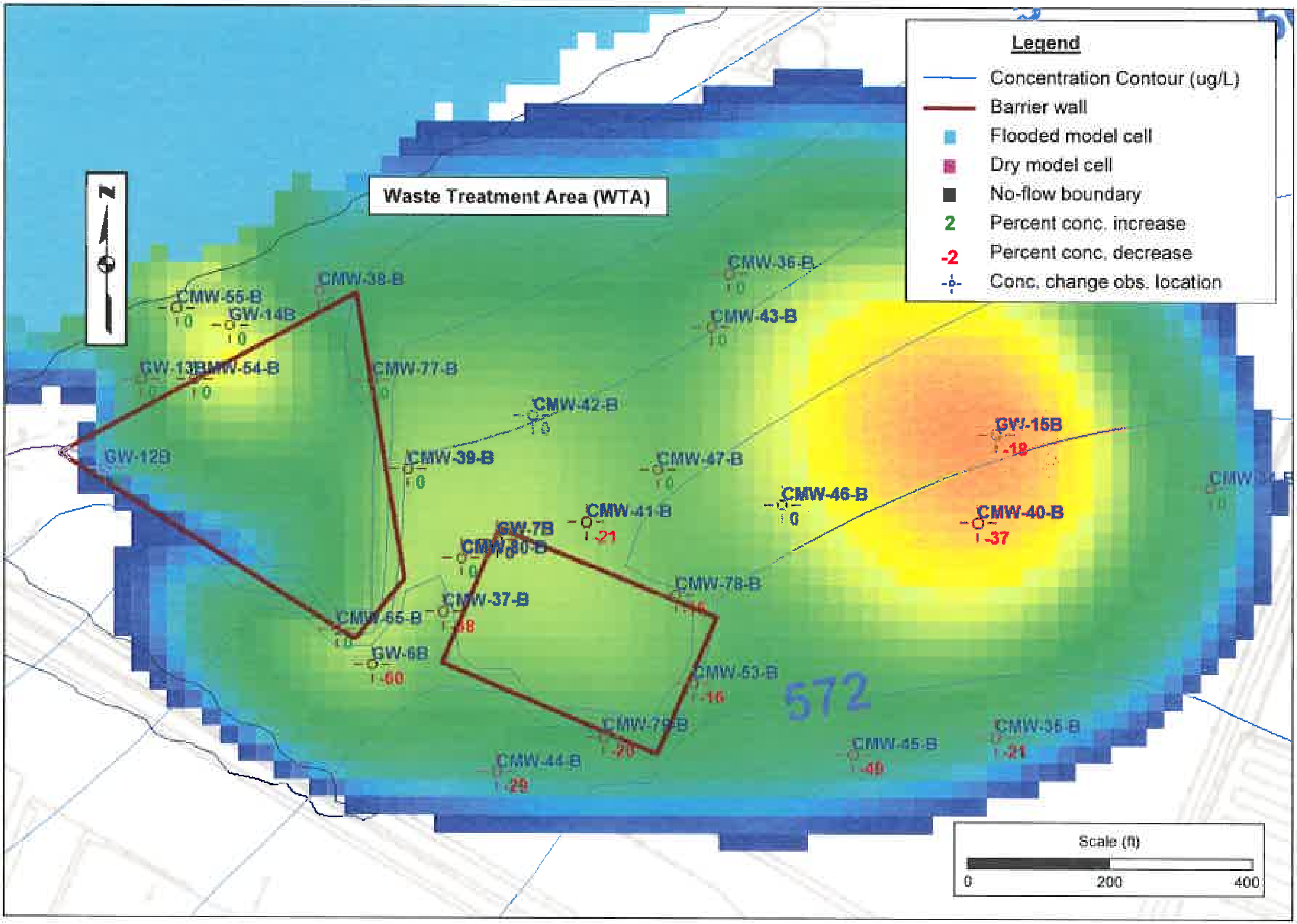
**Figure 13**
**Simulated Percent VOC Concentration Change in Zone B Over 3 Years a the WTA**



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## Figure 14
## Proposed Locations of Concentration Wells for Effectiveness Monitoring